

UNCLASSIFIED

AD-A204 802

REPORT DOCUMENTATION PAGE

DTIC FILE

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		1b. RESTRICTIVE MARKINGS	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.	
6a. NAME OF PERFORMING ORGANIZATION Naval Ocean Systems Center	6b. OFFICE SYMBOL (if applicable) NOSC	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State and ZIP Code) San Diego, CA 92152-5000		7b. ADDRESS (City, State and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Ship Research/Development Center	8b. OFFICE SYMBOL (if applicable) DTNSRDC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
9c. ADDRESS (City, State and ZIP Code) David Taylor Labs Annapolis, MD 21402		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. AGENCY ACCESSION NO. 63724N ME38 DN888 749	
11. TITLE (Include Security Classification) INCREASED SENSITIVITY IN MEASUREMENT OF BUTYLTINS IN SEAWATER			
12. PERSONAL AUTHOR(S) M. O. Stallard, P. F. Seligman, C. Clavell			
13a. TYPE OF REPORT Presentation/Speech	13b. TIME COVERED FROM June 1988 TO June 1988	14. DATE OF REPORT (Year, Month, Day) November 1988	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) CIVAPP Marine fouling CIVAPP environmental impact statement, <i>tin compounds, butyl iodide, n-butyl</i>	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This study describes modifications to an existing method for measuring n-butyltins that result in greatly increased sensitivity. The absolute detection limits of the cationic species are 80-180 pg. This increased sensitivity, yielding a 0.2-0.4 ng/L environmental detection limit is achieved by using a closed end quartz furnace and silanizing the glass cryogenic trap.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE PERSON P. F. Seligman		22b. TELEPHONE (include Area Code) (619) 553-2775	22c. OFFICE SYMBOL Code 522

Presented at the American Chemical Society Organometallics in the Environment Symposium, 5-11 June 1988, Toronto, Canada

DTIC
ELECTE
S 14 FEB 1989
E

80 2 14 002

INCREASED SENSITIVITY IN MEASUREMENT OF BUTYLTINS IN SEAWATER
Martha O. Stallard Computer Sciences Corporation, San Diego, CA
92110 U.S.A., Cesar Clavell and Peter F. Seligman, Naval Ocean Systems
Center, San Diego, CA 92152-5000 U.S.A.

This study describes modifications to an existing method for measuring n-butytlins that result in greatly increased sensitivity. The absolute detection limits of the cationic species are 80-180 pg. This increased sensitivity, yielding a 0.2-0.4 ng/L environmental detection limit is achieved by using a closed end quartz furnace and silanizing the glass cryogenic trap.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



"PREPRINT EXTENDED ABSTRACT"
Presented Before the Division of Environmental Chemistry
American Chemical Society

Toronto, Canada

June 5-11, 1988

INCREASED SENSITIVITY IN MEASUREMENT
OF BUTYLTINS IN SEAWATER

Martha O. Stallard
Computer Sciences Corporation
San Diego, CA 92110 U. S. A.

Peter F. Seligman and Cesar Clavell
Naval Ocean Systems Center
San Diego, CA 92152-5000 U. S. A.

Increasing controversy over the use of tributyltin based antifouling paints and its impact on the marine environment has made the development of techniques to measure part per trillion (ng/L) levels necessary. Modifications of the method developed by Hodge, et. al. [1] and the Naval Ocean Systems Center [2,3] have increased the sensitivity by a factor of ten, from 4 ng/L to 0.4 ng/L for (n-Bu)₃ Sn. It is evident from work by Donard, et. al. [4] that the design of the quartz burner can influence sensitivity. A closed end quartz furnace was found to give optimum sensitivity in our work.

The optimized system consists of a modified 500 ml gas washing bottle (hydride generator) with an outlet on the top and an injection port on the side. Teflon tape is wrapped around 1/8 inch O.D. teflon tubing to form a secure seal when the tubing is threaded through the top outlet. This tubing is then pressure fit into the end of a 3mm I. D. glass U tube (2 1/2-3 inch sides) which forms the cryogenic trap for the tin hydrides. Avoiding the use of Swagelok fittings improves the analysis. It is important that the glass traps be thoroughly clean and the active sites which complex the hydrides and cause peak reduction or broadening be sealed. The traps are cleaned by soaking in hot 20% Pierce RBS 35 in distilled water rinsed and dried. The traps are washed with hexane and methanol and dried in a 110° oven. While still warm they are filled with silanizing fluid (Supelco Silon CT) and allowed to sit for thirty minutes. The traps are then thoroughly flushed with hexane and methanol and dried in a 200° oven for 10 minutes. Twenty to thirty milligrams of 3% OV-1 on 80/100 chromsorb W HP are added and secured with silanized glass wool plugs.

The trap is connected to the quartz burner with another teflon tube fitted with a glass capillary tip. The tip is positioned at the edge of the barrel of the burner and the tubing secured by a Swagelok reduction fitting.

Samples are analyzed by hydride derivatization and hydrogen flame atomic absorption spectroscopy using parameters previously described [3]. The quartz burner design concentrates the evolved tin

hydrides in a small area resulting in an intensified signal. All lines and the trap were periodically flushed with dry helium to remove water vapor. This is important to retain sensitivity and increase the life of the trap. The traps must be thoroughly dried with helium purging between runs. Figure 2 shows typical results of the analysis of a seawater sample with fairly low butyltin concentrations. The absolute detection limits were obtained by running a series of blank seawater samples spiked with 0.5 ng each of mono, di, and tri-butyltin chloride. The detection limits based on 3 σ of these near background standard additions are 180 pg tributyltin, 80 pg dibutyltin and 120 pg monobutyltin calculated as the cation.

References

1. Hodge, V. F.; Seidel, S. L.; Goldberg, E. D.; Anal. Chem. 1979, 51, 1256-1259
2. Valkirs, A. O.; Seligman, P. F.; Vafa G.; Stang P. M.; Homer, V.; Lieberman S. H.; Naval Ocean Systems Center Technical Report 1037 1985
3. Valkirs, A. O.; Seligman, P. F.; Olsen G.; Brinckman, F. E.; Matthias, D. L.; Bellama, J. M.; Analyst 1987, 112, 17-21
4. Donard, O. F.; Rapsomanikis, S.; Weber, J. H.; Anal. Chem. 1986, 58 772-777

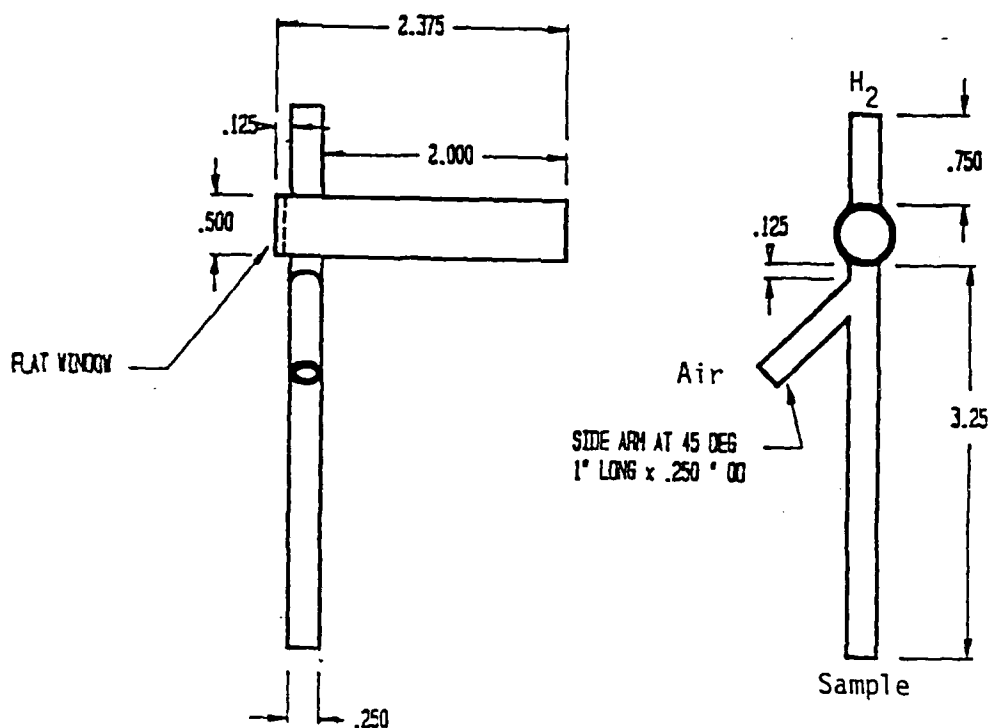


FIGURE 1. CLOSED END QUARTZ BURNER (DIMENSIONS IN INCHES)

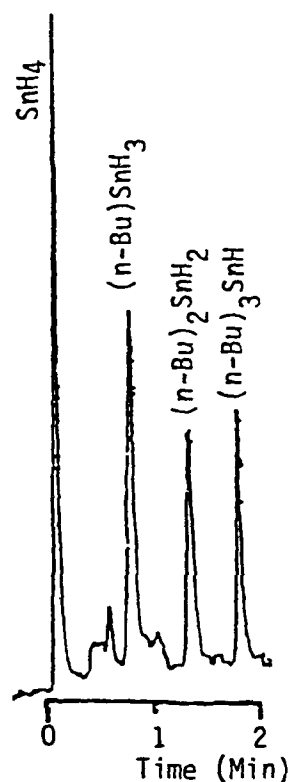


FIGURE 2. SPECIATION OF BUTYLTINS IN SEAWATER. AMOUNT OF COMPOUNDS AS THE CATION IS AS FOLLOWS $(n\text{-Bu})\text{Sn}^{+3}$ 1.3ng
 $(n\text{-Bu})_2\text{Sn}^{+2}$.64ng $(n\text{-Bu})_3\text{Sn}^{+}$ 1.3ng